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(71) Applicant (for all designated States except US): **A.L.T. ADVANCED LASER TECHNOLOGIES LTD.** (IL/IL);
Old Industrial Zone, 10550 Migdal Haemek (IL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BROOK-LEVINSOHN, Edward** (IL/IL); 11 Hana Senesh Street, 49507 Petah Tikva 49507 (IL). **KOGAN, Michael** (IL/IL); 9 Havradim Street, 20306 Nesher (IL).

(74) Agent: **REINHOLD COHN AND PARTNERS**; P.O.B. 4060, 61040 Tel Aviv (IL).

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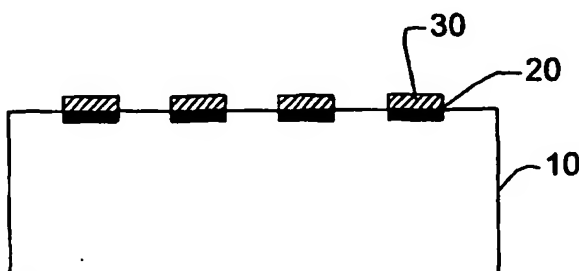
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(54) Title: METHOD FOR THE FORMATION OF A PATTERN ON AN INSULATING SUBSTRATE



(57) Abstract: The present invention provides a method of forming a pattern on an insulating substrate, the method comprising the steps of: providing an insulating substrate made of organic polymer, and treating the substrate with a laser beam so as to irradiate selective portions of the substrate in accordance with the pattern to be formed. Upon laser treatment, the irradiated portions of the substrate undergo a modification, for example undergo ablation and/or become conductive due to carbonization and/or graphitization of the substrate material. The method of the invention may be used in the manufacture of printed circuit boards. In such cases, the laser treated substrate is further exposed to an electroless metal plating step

and/or to a galvanic deposition step for the selective deposition of metal on the irradiated areas.

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METHOD FOR THE FORMATION OF A PATTERN ON AN INSULATING SUBSTRATE

FIELD OF THE INVENTION

The present invention relates to a method for the formation of a pattern on a substrate surface and more particularly to the use of such method in the fabrication of printed circuit boards.

5 BACKGROUND OF THE INVENTION

A printed circuit board (PCB) usually consists of a substrate made of dielectric material such as epoxy, polyimide or the like, typically glass-reinforced, carrying a pattern of conductors on one or both of its surfaces.

Numerous techniques have been developed for forming the conductor
10 pattern of PCBs. At present, these patterns are effected almost exclusively with photosensitive coatings referred to as photoresists. Depending on their chemical structure, they may serve as either negative or positive resists, i.e. may either polymerize (harden) or decompose into soluble constituents upon exposure to high energy radiation.

15 For PCB technology with geometries on the order of mils, UV photolithography is the most common used process. In such process the imagewise exposure of the photoresist film, i.e., the exposure of only selected portions of it to UV light irradiation to produce the desired latent image, is predominantly effected with an appropriately patterned mask (phototool) which permits passage of UV
20 light therethrough to the film, only in the desired locations. After exposure the

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latent image can be developed to provide the desired resist pattern.

In recent years, attention has been directed to so-called "direct imaging" techniques, employed in the production of both PCBs and printing plates. In these techniques, the exposure of selected areas of the resist film to the activating
5 radiation needed to bring about the required changes in the film composition does not utilize a radiation source directed through a mask, but rather employs a suitably focused laser beam of appropriate wavelength light, which directly scans the resist film in a predetermined, computer-controlled, manner - see, for example, U.S. Patent No. 4,724,465 and US Patent No. 6,090,529. While such
10 techniques offer potential advantages in resolution capability and avoidance of defects sometimes caused by imperfect phototool artwork and/or by operator handling of phototools, those developed to date are too slow for mass production and require expensive resists

The above methods involve a considerable number of steps, making them
15 time-consuming and expensive.

A method for manufacturing a resistance element on the surface of a non-conductive layer is described in US 4,489,230. In this method, the base layer is irradiated by a laser beam through a laser beam transmitting film. The irradiated portions of the base layer are carbonized, thereby forming resistance elements, i.e.
20 elements of high electrical resistance, used in an electric or electronic circuit.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a simplified method for forming a desired pattern on an insulating substrate without reliance upon
25 photosensitive materials or compositions, thus obviating the use of numerous operational steps.

A further object of the present invention is to provide a simplified method for producing conductive pathways on an insulating substrate.

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Thus, the present invention provides a method of forming a pattern on an insulating substrate, the method comprising the steps of:

- a) providing an electrically-insulating substrate made of organic polymer;
 - b) treating the substrate with a laser beam so as to irradiate selective portions of the substrate in accordance with the pattern to be formed, the laser beam being capable of modifying the irradiated portions of said substrate, thus forming a pattern of modified areas spaced by insulating areas of the substrate. The irradiated portions of the substrate undergo a modification upon the laser treatment, for example they become more conductive, due to carbonization and/or graphitization.
- 10 The substrate is exposed to a laser beam either through a mask capable to selectively transmit the laser beam or scanned in a direct write technique, i.e. a software program drives a laser beam in a predetermined, desired manner.

According to another aspect, the present invention provides a method for manufacturing a printed circuit board (PCB), the method comprising the steps of:

- a) providing an electrically-insulating substrate made of organic polymer;
- b) treating said substrate with a laser beam so as to irradiate selective portions of the substrate in accordance with the pattern to be formed, the laser beam being capable of modifying the irradiated portions of said substrate, thus forming a pattern of modified areas spaced by insulating areas of the substrate; and
- c) coating said modified areas obtained in step b) above with a metal layer so as to obtain a conductor circuit pattern.

According to a preferred embodiment, the irradiated portions of the substrate undergo carbonization and/or graphitization, thus forming a pattern of carbonized and /or graphitized, conductive areas spaced by insulating areas

The PCB produced by the above method constitutes a further aspect of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

In order to understand the invention and to see how it may be carried out in practice, a preferred embodiment will now be described, by way of non-limiting example only, with reference to the accompanying drawings, in which:

5 **Fig. 1** is a schematic representation of a known photolithographic process.

Fig. 2A is a schematic representation of a substrate processed by the method of the invention.

Fig. 2B is a schematic representation of a substrate processed by the method of the invention, which was further exposed to a metal deposition step.

10 DETAILED DESCRIPTION OF THE INVENTION

The basic steps of a known photolithographic process for producing a PCB are outlined in **Fig.1**. A photoresist material is applied as a thin coating over a dielectric substrate, for example epoxy substrate, having a metal layer (e.g. copper) covering one or both of its faces. The resist material is exposed in an imagewise
15 fashion (through a mask) such that light strikes selected areas of the resist material. Depending upon the chemical nature of the resist material, the exposed areas may be rendered more soluble in a developing solvent than the unexposed areas, thereby producing a positive image of the mask. Conversely, the exposed areas may be rendered less soluble producing a negative image of the mask. The metal areas not
20 protected by resist are etched down to the dielectric substrate surface, whereupon subsequent removal of the resist reveals the desired conductor pattern. Other common techniques include activation and metal deposition steps after the treatment with a developing solvent.

From the above description it is clear that known methods for producing
25 PCBs involve numerous steps, making them time-consuming and expensive, especially in comparison to the present invention.

According to the present invention, the irradiating laser beam causes modification of irradiated portions of the substrate. Such modification consists in physical and/or chemical change of the substrate material, for example ablation or

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transformation of the irradiated areas of the substrate into areas having significantly higher conductivity compared to the insulating substrate made of organic polymer.

The laser beam selectively forms a desired pattern in the substrate by causing carbonization and/or graphitization and/or ablation of the organic material of the substrate only in irradiated areas. A schematic representation of a substrate processed by the method of the present invention is showed in Fig. 2A. Thus, a polymeric substrate 1 is irradiated by a focused laser beam which generates very high temperatures in the irradiated regions, so that the substrate is modified in those regions. The modified regions 2 of the substrate preferably become conductive due to the formation of carbonized and/or graphitized structures. Depending on the substrate used, the depth of the carbonized and/or graphitized and/or ablated areas of the substrate ranges from about 1 μm to about 200 μm , preferably from 1 μm to about 20 μm . The term "carbonization and/or graphitization process" used herein describes a process where heating permits the transformation of organic material into carbonized or graphitized structures or any mixtures thereof.

Organic material is usually carbonized at temperatures in the range of 800-1200°C and graphitized at higher temperatures, in the range of 1200-3500°C. The physical properties of carbonized material are different than those of graphitized material since carbon is amorphous and has high electrical resistance, while graphite is a crystalline material with hexagonal structure, possesses relatively low electrical resistance or relatively high electrical conductivity. Mixtures of carbonized and graphitized material include a wide range of materials varying in conductivity and varying in structure.

The substrate may be exposed to the laser beam either through a mask capable to transmit the laser beam or in a direct write mode, i.e. the laser beam being conducted by a software program in a predetermined, desired manner. The preferred source of high energy required for the carbonization and/or graphitization process and/or ablation is a laser capable of producing thermal energy, such as diode, carbon dioxide laser or Neodymium-Yag laser, etc. For industrial-scale production of products such as PCBs, where speed of processing is of high

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importance, energy sources of high intensity will be preferred, such that the required chemical transformation of the substrate material occurs in a rapid manner.

In a most preferred embodiment of the invention, the method of the invention enables the fabrication of PCBs, obviating the use of photoresists and processing steps related thereto. Fig. 2B schematically illustrates a substrate which was processed according to the present invention and further exposed to a metal deposition step so as to form a conductive pattern, for example a PCB. The laser beam supplies a highly localized heat which induces carbonization and/or graphitization and/or ablation. Thus, a dielectric substrate 10 is exposed to a laser beam which supplies a highly localized heat which induces carbonization and/or graphitization and/or ablation to produce a desired pattern of modified regions 20 spaced apart by insulating regions of the substrate. Suitable substrates for use in the process of the present invention are polymeric materials used as substrates in the PCB industry. Non-limiting examples of such polymeric materials are epoxy polymers, polyesters, polyimides, liquid crystal polymers (LCP), or fluoropolymers. In order to increase the absorption of energy supplied by the laser, the polymeric substrate may comprise various additives, for example dyes, pigments, binders and fillers.

After laser exposure, the patterned substrate is subjected to a coating procedure. The coating may be carried out by known processes, for example by placing the substrate in a standard electroless deposition bath and/or by subjecting it to an electroplating process so as to obtain areas 30 of metal (e.g. copper) deposition on the modified, preferably conductive, areas of the substrate.

In the fabrication of PCBs, the laser beam may have a dual function, namely forming a pattern of modified areas spaced apart by insulating areas and during the same operation, also drilling necessary holes through the substrate, thus enabling the formation of vias. The walls of the vias are then provided with a metal coat during the electroless plating and/or electroplating of the entire patterned substrate, as explained above, so as to establish electrical conduction between the top and bottom of each via.

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The process described above has been employed to produce patterns with resolution of 1 mil or even less.

The process of the present invention is further illustrated hereinafter with reference to some non-limiting Examples.

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EXPERIMENTAL

Substrates: standard materials used in the preparation of PCBs by conventional technology. Examples of such materials are epoxy glass (FR-4) having a
10 thickness of 1.5 mm, or polyimide films (Kapton) having a thickness of 180 microns.

Laser source: Nd:YAG laser having a wavelength of 1064 nm, impulse frequency from 0 to 75 kHz, impulse duration of 70ns-100 μ s, power 3W-CW,
15 and pulse energy for kHz: 3mJ.

Laser Treatment: The treatment was carried out in the air or under an inert atmosphere, with a scanning rate ranging from 5 to 200 m/min. The selected laser treatment mode provided ablation of the surface layer of the substrate to a depth
20 of ~0.01-100 μ m. The treated zone had the form of straight grooves and any required length.

Chemical Treatment: after laser irradiation, the surfaces of the grooves were subjected to electroless plating for obtaining thick layers of copper on the
25 surfaces of the grooves. Before the metal deposition the irradiated surfaces were subjected to at least one of the following pretreatments: a) activation with PdCl₂ 5-10 g/l; b) sensibilization with a solution containing 10-50 g/l SnCl₂ and 10-15 ml/l HCl, and c) treating with an ammonium solution of copper hypophosphite.

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The electroless plating solution contained:

- Copper sulfate – 25-35 g/l
- TRILON B – 80-90 g/l
- Sodium hydroxide – 30-40 g/l
- 5 Sodium carbonate – 20-30 g/l
- Stabilizers – 0.1-0.15 g/l
- Formaldehyde (sol. 40%) – 20-25 ml/l

The pH of the above solution was 12.6-12.8. The copper deposition process was carried out during various periods of time, from several minutes to a
10 few hours, to obtain copper conductors having a thickness of up to 50-60 μ .

In order to obtain layers of copper with a higher thickness, the coating was carried out by a combined chemical and galvanic method called the Acid Copper Plating (ACP) method. ACP was carried out in a solution regularly used for
15 acidic deposition of copper coatings. The composition and other parameters of the solution and the process were as follows:

- Copper sulphate 230.0 g/l
- Sulfuric acid 50 g/l
- Sodium chloride 30 mg/l
- 20 Temperature 25°C
- Current 3 A/dm².

The current value was calculated according to the total surface area of the substrate to be coated. The copper deposition lasted for 20 min.

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Results

Grooves were formed upon subjecting a substrate, for example an epoxy glass substrate or polyimide substrate such as KAPTON, to laser treatment. As a result, a graphite layer was formed on the internal surface of the grooves and their edges. The width of the groove, depending on the irradiation mode, achieved 10 to 150 μm .

The specific electrical resistance of the graphite layer formed upon laser irradiation was approx. 220 Ohm*cm while that of the epoxy glass was $10^9 \div 10^{10}$ Ohm*cm.

The irradiated portions were subjected to a plating process, using acid copper plating process and a layer of electrolytic copper was formed on the surface of the modified (graphitized) layer, having a thickness of several microns to a few dozen microns.

One of the important characteristics of a conductive pattern prepared by the method of the present invention, is the adhesion in substrate-graphite and graphite-copper systems.

To determine the adhesion, the following study was carried out: a copper wire having a diameter of 0.2 mm was soldered to the surface using tin solder. After that, a peeling test was carried out. The surface area of the contact between the copper and the substrate was approximately constant and equaled $\sim 0.03 \text{ cm}^2$. The results of the tests are presented in Table 1.

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Table 1. Results of the peeling test for different samples.

No	Substrate Material	Peeling Force, g	Boundary	Specific Peeling Force, g/cm ²
1.	Epoxy Glass	60	Epoxy/graphite	2000
2.	Epoxy Glass	50	epoxy/graphite	1700
3.	Epoxy Glass	320	graphite/copper	10700
4.	Epoxy Glass	340	graphite/copper	11300
5.	Graphite Electrode	400	graphite/copper	13300
6.	Copper	464	tin/copper	15500

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The present invention has been described with a certain degree of particularity, but those versed in the art will readily appreciate that various alterations and modifications may be carried out without departing from the scope of the following claims.

CLAIMS:

1. A method of forming a pattern on an insulating substrate, the method comprising the steps of:
 - a) providing an insulating substrate made of organic polymer;
 - 5 b) treating said substrate with a laser beam so as to irradiate selective portions of the substrate in accordance with the pattern to be formed, the laser beam being capable of modifying the irradiated portions of said substrate, thus forming a pattern of modified areas spaced by insulating areas of the substrate.
- 10 2. A method according to claim 1, wherein said irradiated portions of the substrate become conductive due to carbonization and/or graphitization of the substrate material.
3. A method according to claim 1 or 2, further comprising subjecting the laser treated substrate to an electroless metal plating step and/or to a galvanic deposition
15 step for the selective deposition of metal.
4. A method according to claim 1, wherein said treating with a laser beam in step b) is carried out through a phototool (mask) corresponding to the pattern to be formed.
5. A method according to claim 1, wherein said treating with a laser beam in step b) is carried out in a predetermined manner, by direct write.
- 20 6. A method of manufacturing a printed circuit board (PCB), the method comprising the steps of:
 - a) providing an insulating substrate made of organic polymer;
 - b) treating said substrate with a laser beam so as to irradiate selective portions of the substrate, the laser beam being capable of modifying the
25 irradiated portions of said substrate, thus forming a pattern of modified areas spaced by insulating areas; and
 - c) coating said modified areas obtained in step b) above with a metal layer so as to obtain a conductor circuit pattern.

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7. A method of manufacturing a printed circuit board (PCB), the method comprising the steps of:

- a) providing an insulating substrate made of organic polymer;
- b) treating said substrate with a laser beam so as to irradiate selective portions of the substrate, the laser beam being capable of carbonizing and/or graphitizing the irradiated portions of said substrate, thus forming a pattern of carbonized and/or graphitized areas spaced by insulating areas; and
- c) coating said carbonized and/or graphitized areas obtained in step b) above with a metal layer so as to obtain a conductor circuit pattern.

8. A method according to claim 6 or 7, wherein said treating with a laser in step b) is carried out through a phototool (mask) corresponding to the pattern to be formed

9. A method according to claim 6 or 7, wherein said treating with a laser beam in step b) is carried out in a predetermined manner, by direct write.

10. A method according to any one of claims 1, 6 or 7, wherein said polymeric substrate is made of epoxy, epoxy glass, polyimides, polyesters, liquid crystal polymers, fluoropolymers or mixtures thereof.

11. A method according to any one of claims 1, 6 or 7, wherein said polymeric substrate further comprises a dye or a pigment.

12. A method according to claim 6 or 7, wherein said metal layer in step c) is made of copper, nickel or mixtures thereof.

13. A method according to claim 6 or 7, further comprising the formation of vias during the exposure of the substrate to a laser beam in step b).

14. A method according to claim 6 or 7, further comprising coating of the vias obtained by the method of claim 13, with a metal coating in step c).

15. A product produced by the method of claim 1 or 2.

16. A printed circuit board produced by the method of claim 6.

17. A printed circuit board produced by the method of claim 7.

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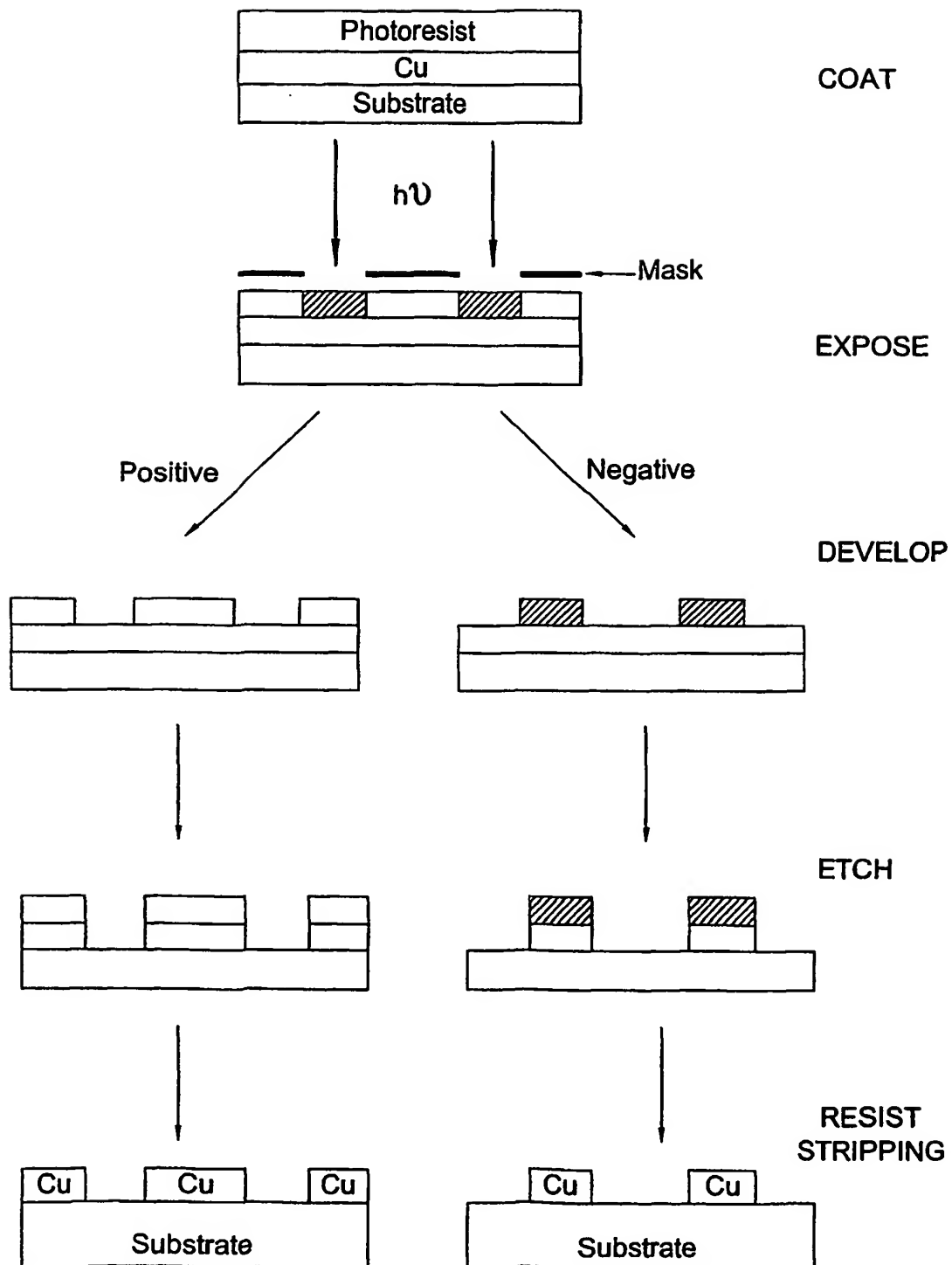


FIG. 1

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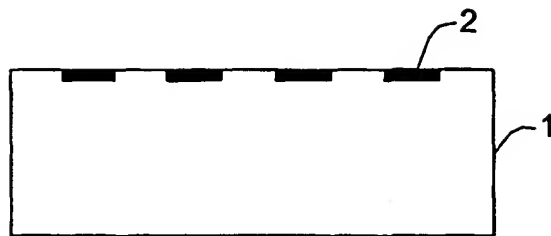


FIG. 2A

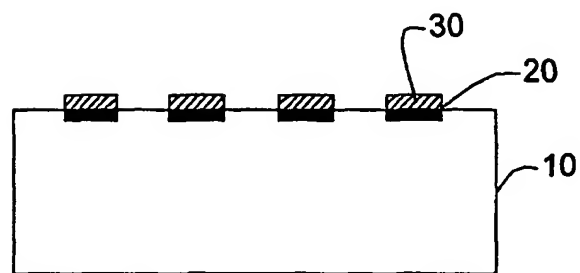


FIG. 2B

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(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

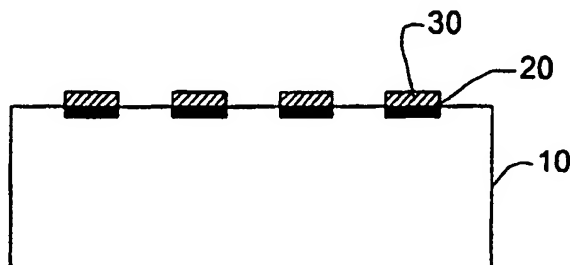
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A. CLASSIFICATION OF SUBJECT MATTER

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, IBM-TDB, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 91 18489 A (OLIN CORP) 28 November 1991 (1991-11-28) page 17, line 17 -page 18, line 14; figures 12,13	1-3,5-7, 9,10, 12-17
Y	---	4,8,11
Y	US 4 900 581 A (STUKE ET AL.) 13 February 1990 (1990-02-13) figure 1	4,8
Y	---	11
A	DE 12 62 395 B (SIEMENS AG) column 3, line 6 - line 8	13,14

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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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